



Argonne  
NATIONAL  
LABORATORY

... for a brighter future



U.S. Department  
of Energy

UChicago ►  
Argonne<sub>LLC</sub>



U.S. DEPARTMENT OF ENERGY

U.S. DEPARTMENT OF  
**ENERGY**

Energy Efficiency &  
Renewable Energy

# Advancing Solid-Solid Interfaces in Li-ion Batteries

PIs: Nenad Markovic and Larry Curtiss

## *ANL Collaborators:*

Sanja Tepavcevic, Yisi Zhu, Dillon Fong, John Freeland,  
Vojislav Stamenkovic and Peter Zapol

Argonne National Laboratory

06/20/2018

**Project Manager:** Tien Duong (DOE/EERE)

Project ID # BAT310

This presentation does not contain any proprietary,  
confidential, or otherwise restricted information

# Overview

## Timeline

- Start: 2016
- Finish: 2019
- 35%

## Budget

- Total project funding
  - DOE share: 1300 K
- FY 16: \$ 100 K
- FY 17: \$ 400 K
- FY 18: \$ 400 K
- FY 19: \$ 400 K

## Barriers

- Barriers addressed
  - Stability
  - Ion transport
  - Efficiency

## Partners

- Interactions/ collaborations
  - Jeff Sakamoto (UM)
  - John Mitchell (ANL)
  - Mercouri Kanatzidis (NU)

# Solid-solid Interfaces in Li-ion Batteries

## General Objective

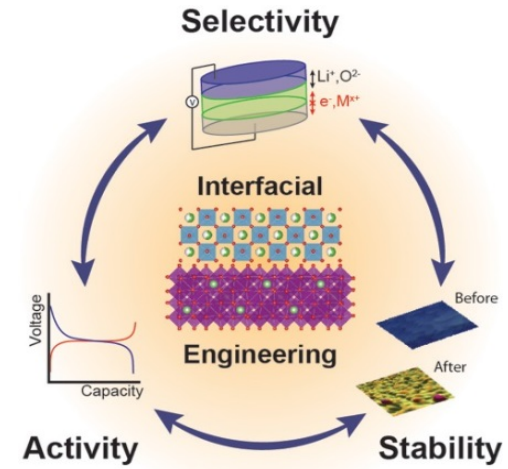
Develop and use state of the art experimental and computational techniques to *establish functional links between activity (cyclability), stability, selectivity and conductivity of electrochemical interfaces and bulk materials in Li-ion battery systems.*

## Strategy

*Science-based approach -fast transfer of fundamental knowledge from model to real world systems.*

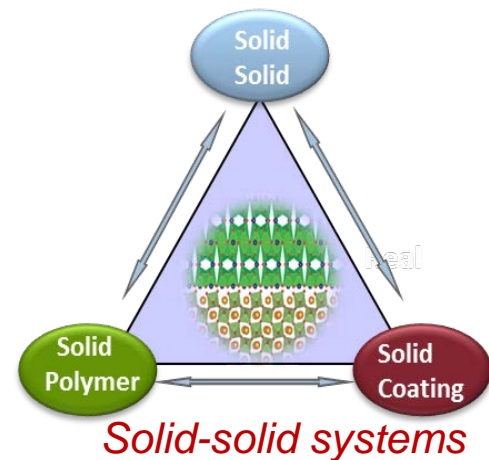
## Systems:

- ✓ All solid-solid battery (solid electrodes and solid electrolytes)



## General Challenge:

- ✓ To develop a mechanically/chemically stable and Li ion conductive ( $\geq 2 \times 10^{-4} \text{ S/cm}$  at 298K) nonflammable solid electrolyte capable of protecting a metal Li anode, and that can operate at cathode potentials  $> 5\text{V}$ .

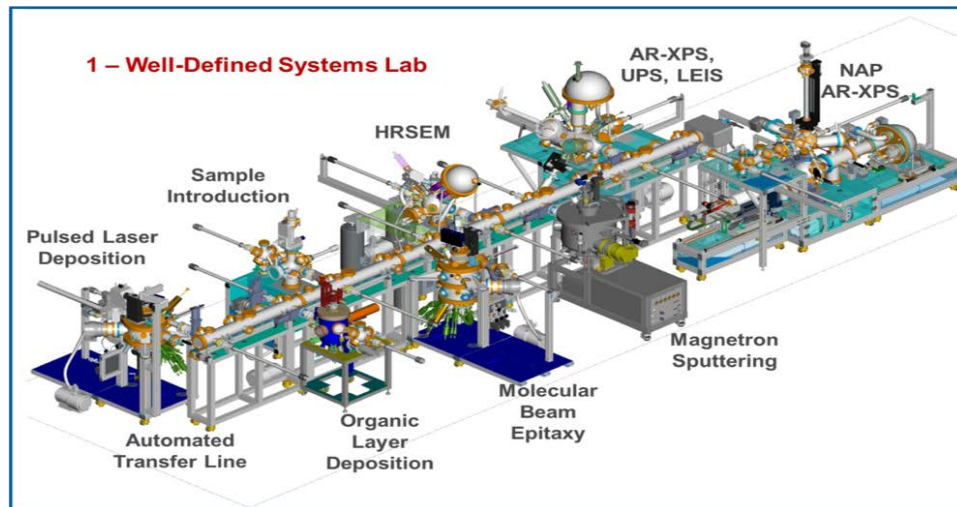


# “Surface Science” Approach

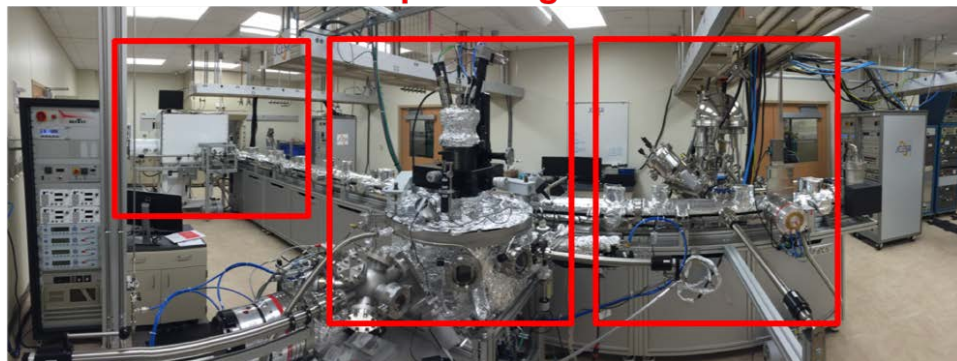
## Synthesis methods

Combination of physical and chemical methods

- ✓ Sputtering
- ✓ Pulse Laser Deposition
- ✓ High throughput modeling
- ✓ Solid Solution
- ✓ Chemical Vapor Deposition
- ✓ Electrochemical



**Glove Box    Sputtering    XPS Chamber**



## Characterization methods

Various ex situ and in situ experimental tools and first principles modeling

- ✓ Low Energy Electron Diffraction
- ✓ X-Ray/Ultraviolet Photoel. Spect.
- ✓ Impedance
- ✓ DFT and molecular dynamics
- ✓ Fourier Transform Infrared Spectroscopy
- ✓ Differential Electroch. Mass Spectrometry
- ✓ Scanning Probe Microscopies
- ✓ Soft X-Ray Spectroscopy

**XAS, XRD  
HAXPES**

**Coin cell  
assembly**



# Milestones

Month/Year	Milestones
Dec/17	Development of new synthesis and characterization methods for controlled deposition of lithium on crystalline LLZMO (M = Nb, Ta, Al) materials on the appropriate substrate. <i>Completed.</i>
Mar/18	Use electrochemical methods to investigate the efficiency as well as charge-discharge cyclability for selected LLZMO materials. <i>Completed.</i>
Jun/18	Development of chemical- and physical-based synthesis method to make amorphous $\text{Li}_2\text{S-P}_2\text{S}_5$ ( $\sim 10^{-3}$ S/cm at room temperature) and LLZMO solid electrolytes with fast ionic transport of Li and elucidate the chemical interaction of Li with such a glass material. <i>On schedule.</i>
Sep/18	Introduce new experimental and computational tools for characterizing ex situ and in situ interaction of Li and $\text{LiCoO}_2$ with amorphous solid electrolytes. <i>On schedule.</i>

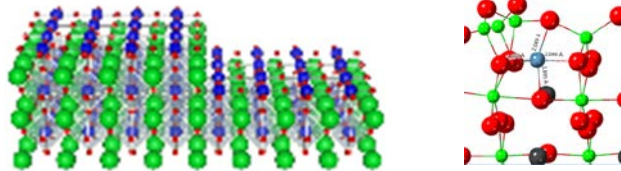




# From Model Systems

## Approach to Interface Reactions:

Li /  $\text{SrTiO}_3$  single crystals



*Atomistic View of Chemical Transformations  
from Experiment/Theory*

## Interface Orientation:

Li/LiCoO<sub>2</sub>

Li/Li<sub>x</sub>La<sub>1-x</sub>TiO<sub>3</sub> (LLTO)

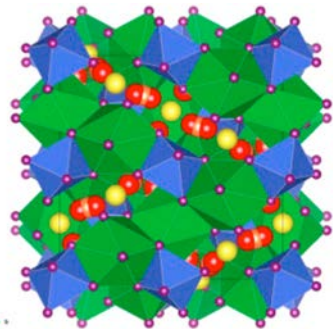


*Interface/bulk Stability and Transport*

## to Real Solid-Solid $\text{S}_{\text{Li}}\text{-S}_{\text{EL}}\text{-S}_{\text{CE}}$

## Interface Reactions and Transport in Oxides

Li /  $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{M}_{0.5}\text{O}_2$  (M = Nb, Ta)    Li /  $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_2$



*Dopants stabilize cubic phase*

*The role of dopants in interfacial properties:*

- Chemical reactivity
- Interface Stability
- Ion Transport

## Interface Reactions in Sulfides

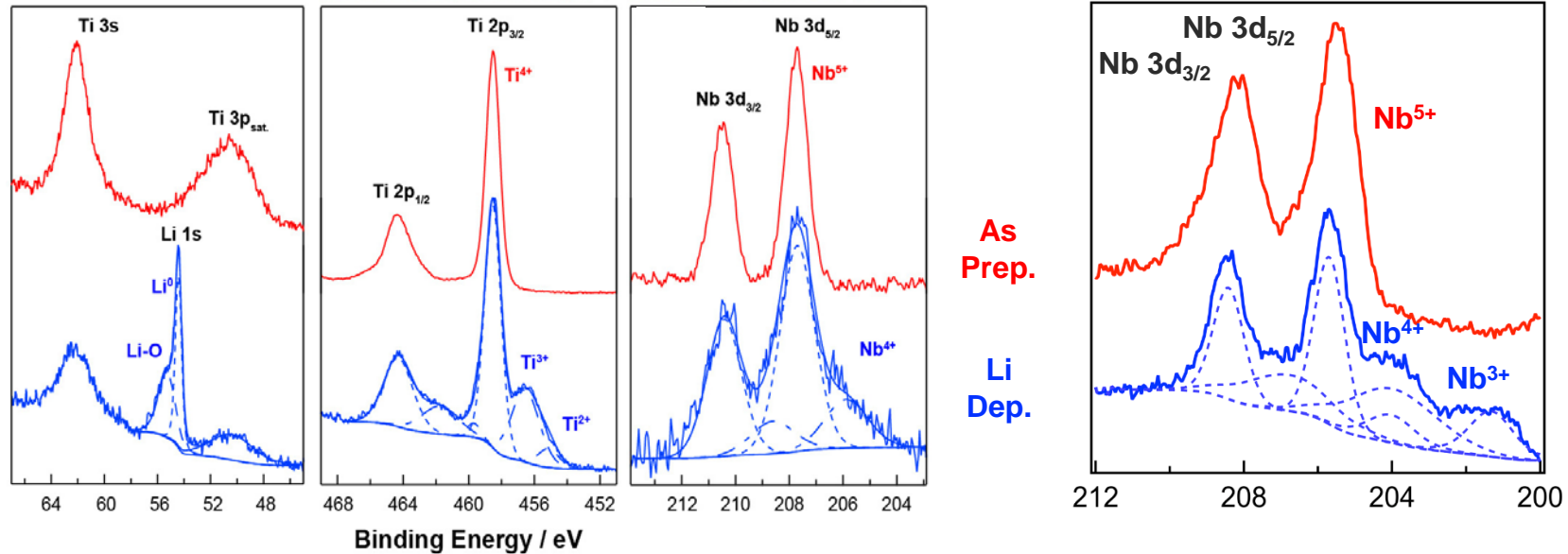
Preliminary  $\text{Li}_3\text{PS}_4$

- The role of phosphorus and sulfur
- Stability of Li-electrolyte interfaces
- Chemical reactivity of disordered interfaces

**Objective:** To develop an atomistic model for minimizing Li-dendrite formation and interfacial/bulk corrosion in real systems

# Example of Li deposited on

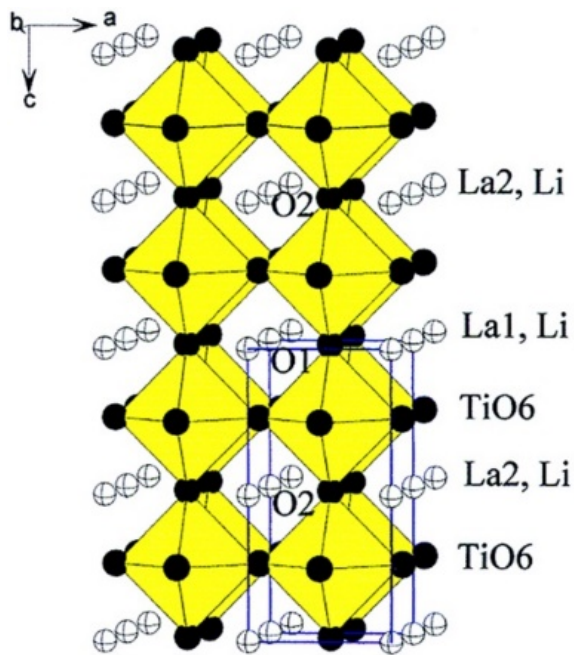
**Model: Nb doped  $\text{SrTiO}_3$  vs Real: Nb doped LLZO**



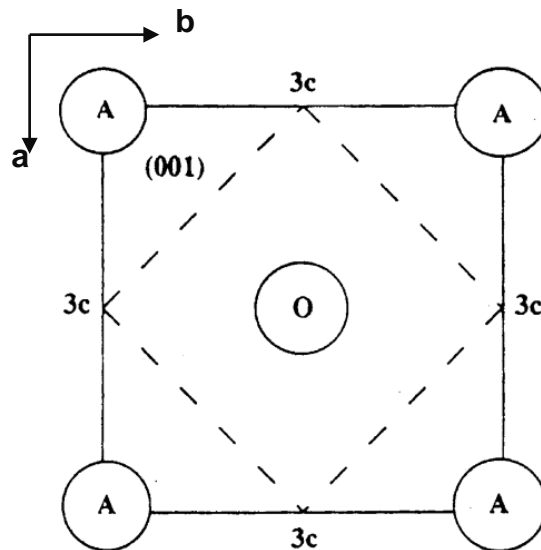
Developed new synthesis and characterization tools for controlled deposition of lithium on solid electrolytes

# Orientation-dependent Li intercalation in LLTO solid electrolyte

## $Li_{0.33}La_{0.55}TiO_3$ (LLTO) structure



Tetragonal ( $c=2a$ )  
Pseudo-Perovskite structure  
with A site vacancies



$Li^+$  intercalate along c-axis

Two pathways:

- (i) from an A site to a 3c site (A-3c-A below)
- (ii) from a 3c site to another 3c site (3c-3c-3c below)

rationalized by the lattice self-potential, site potential, and lattice energy calculation.

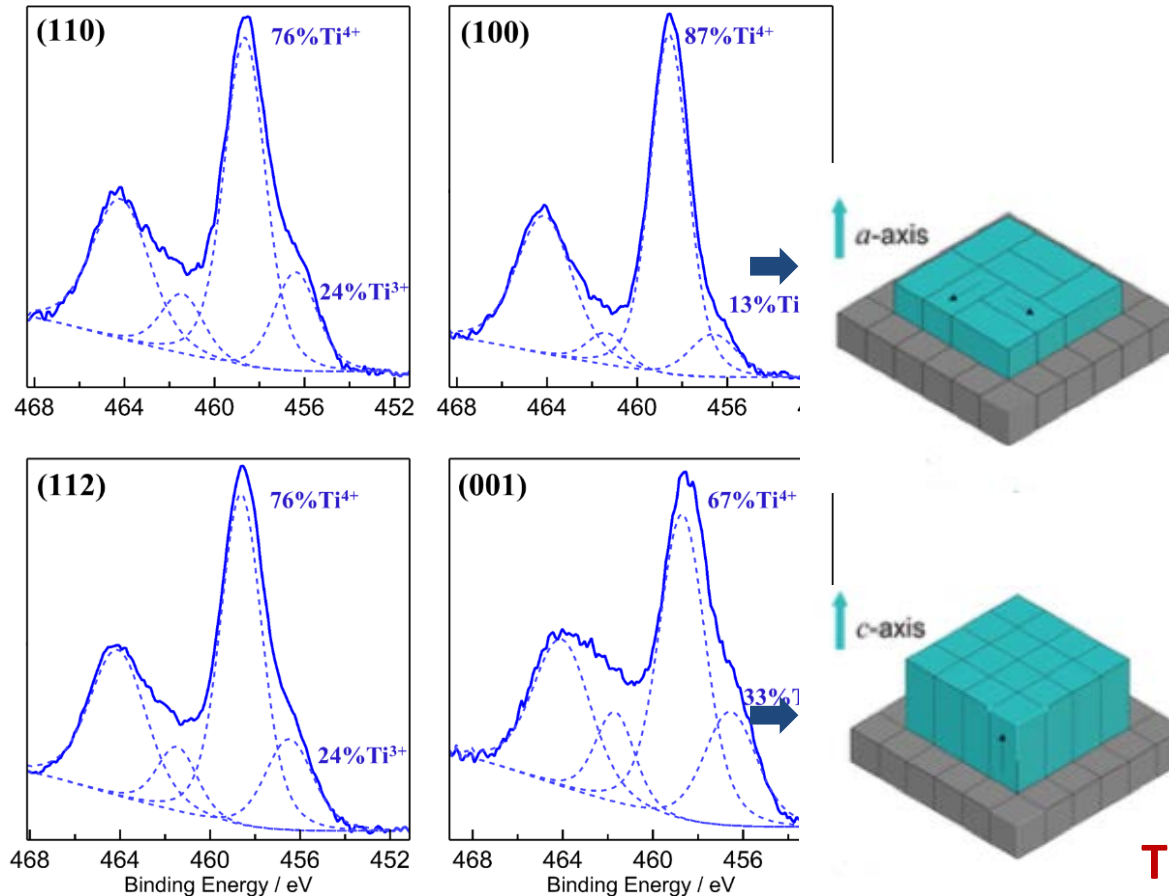
- Sample list
- 1) LLTO(100) || STO(100)
  - 2) LLTO(001) || NGO(110)
  - 3) LLTO(110) || STO(110)
  - 4) LLTO(112) || STO(111)





# Orientation-dependent Li intercalation in LLTO solid electrolyte

## *Ti valence change in the bulk characterized with HAXPES*



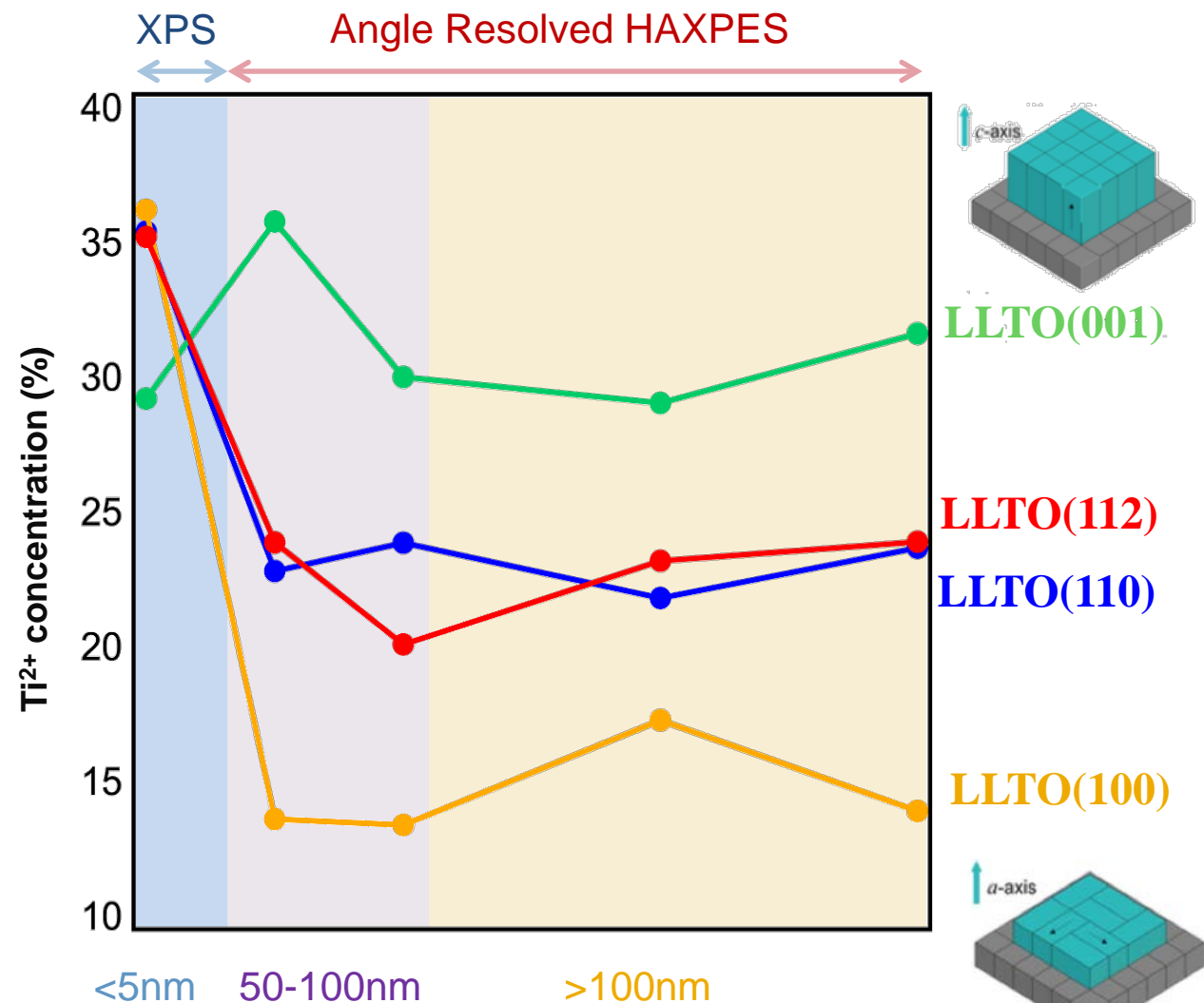
- Ti<sup>4+</sup> in the bulk partially reduced to Ti<sup>3+</sup>
- (100) orientation has the least amount of reduced Ti
- (001) orientation has the largest amount of reduced Ti

Ti 2p HAXPES core level spectra after Li sputtering showed reduction of Ti.

**The amount of reduced Ti in LLTO is highly dependent on orientation**

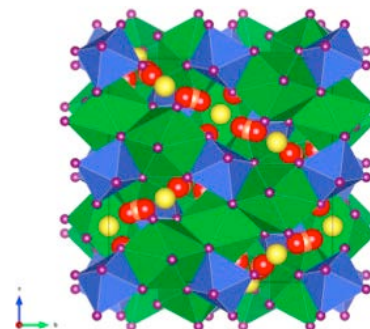
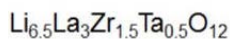
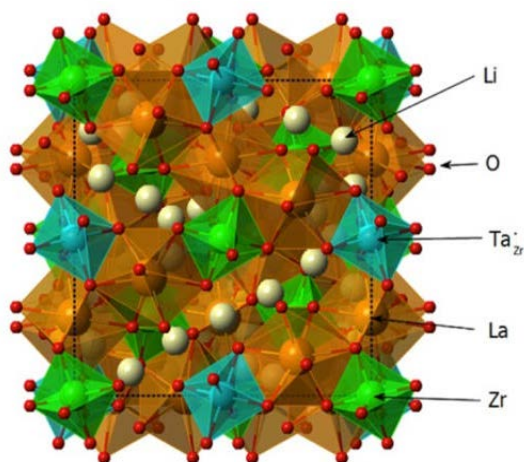
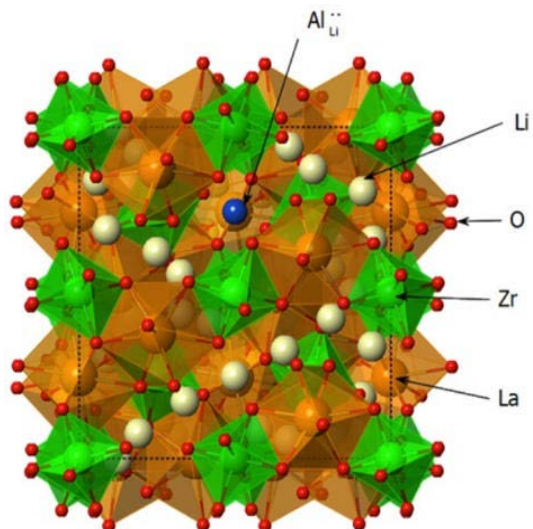
# Orientation-dependent Li intercalation in LLTO solid electrolyte

## Depth profile of $Ti^{3+}$ concentration



- For (001) oriented LLTO, Surface  $Ti^{3+}$  concentration is similar to the bulk → faster Li diffusion path along c-axis
- For other orientations, Surface  $Ti^{3+}$  concentration is higher than the bulk → slower Li diffusion path
- Among them, LLTO(100) has the slowest Li diffusion into the bulk as the fast pathways are in the plane of the surface.

**Higher reactivity in LLTO correlates with faster diffusion: need to optimize both together**



*Garnet type  
LLZO*

- Promising solid electrolyte material with  $\sim 1 \text{ mS cm}^{-1}$  room temperature  $\text{Li}^+$  conductivity
- Conductive cubic phase is stabilized by doping to create Li vacancies via direct (**Al**) or supervalent (**Nb**, **Ta**) substitution

## Technical Challenges

- Uncertainties about interfacial reactivity due to air sensitivity ( $\text{Li}_2\text{CO}_3$  formation)
- Relative stability of material with different dopant species is unknown

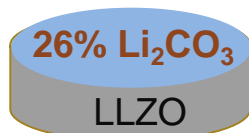
# Intrinsic Reactivity of Real Materials

## *Doped LLZO*



Keep in glove box

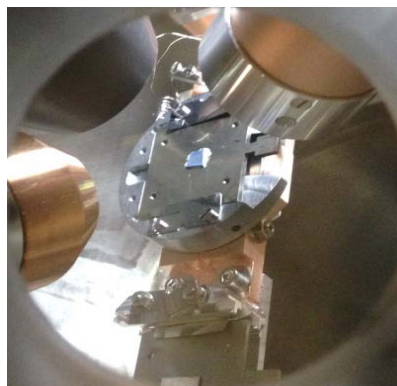
### Unpolished



### Polished



### UHV Annealed



## Oxidation of LLZO

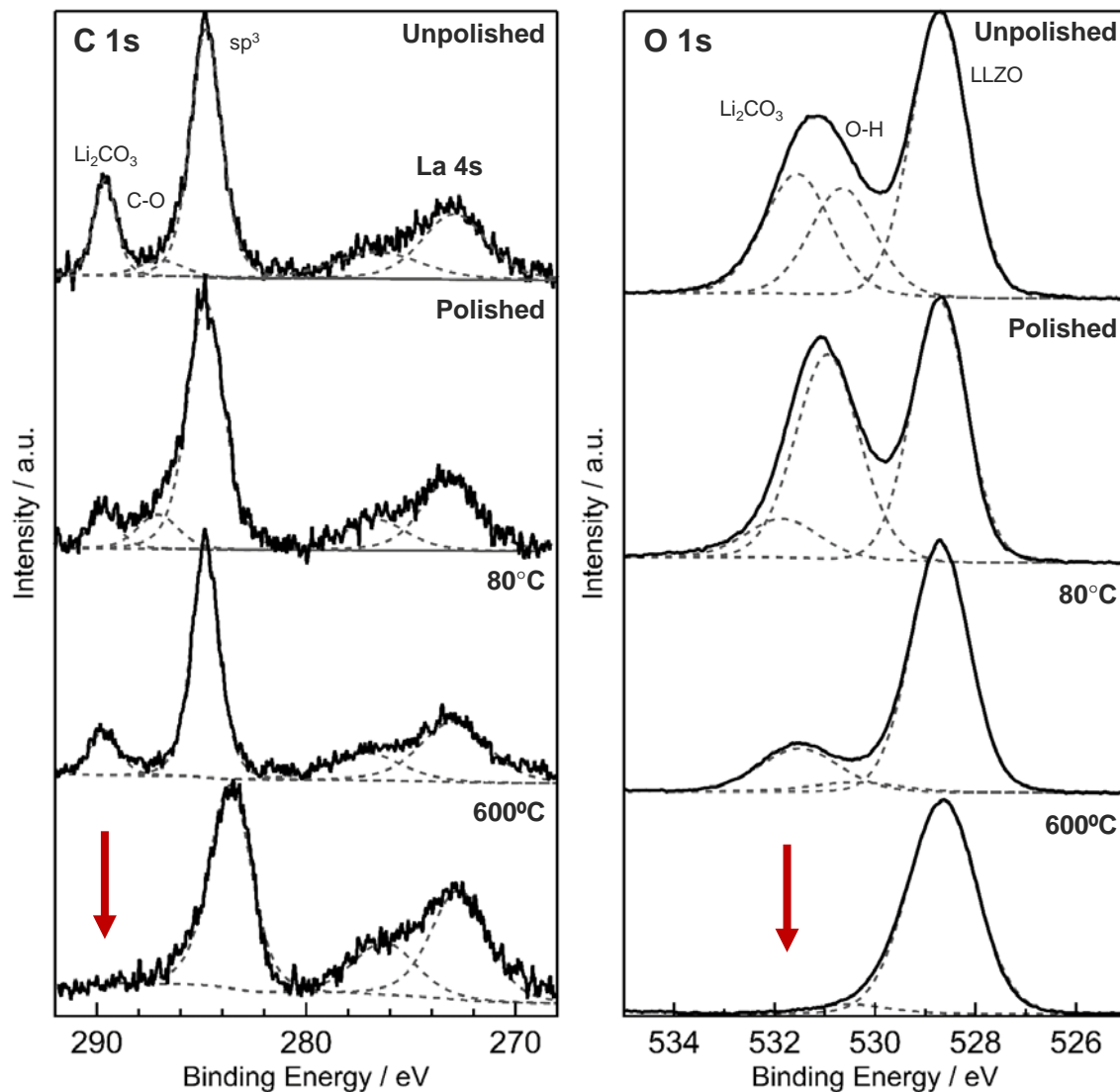
- LLZO quickly oxidizes even in glove box (O<sub>2</sub> & H<sub>2</sub>O < 0.5ppm)
- Oxidation at LLZO surface creates Li<sub>2</sub>CO<sub>3</sub> oxidation layer, which dramatically increases Li/LLZO interfacial impedance
- Previous studies of LLZO/Li interface could not completely remove the oxidation layer on LLZO before contact with Li
- There is a **knowledge gap** in interfacial properties of a non-oxidized LLZO against Li

## Surface Properties

- Unpolished surface:  
Oxidized in glove box mostly covered by Li<sub>2</sub>CO<sub>3</sub>
- Polished surface:  
Li<sub>2</sub>CO<sub>3</sub> mostly removed: < 10%
- UHV annealed surface:  
Li<sub>2</sub>CO<sub>3</sub> totally removed: < Detection Limit

# Intrinsic Reactivity of Real Materials

## LLZO ( $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ )

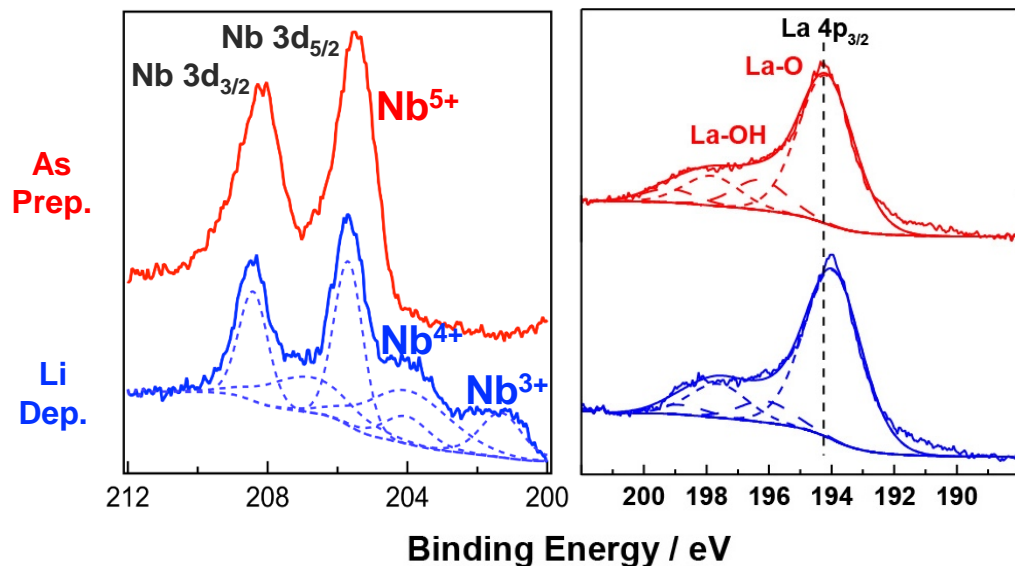


- Surface chemistry of LLZO is strongly dependent on surface pretreatment
- Significant fraction of surface OH groups remains even after polishing in  $\text{H}_2\text{O}$ -free (<0.5 ppm) environment
- XPS shows that annealing in UHV removes residual surface hydroxide and carbonate species

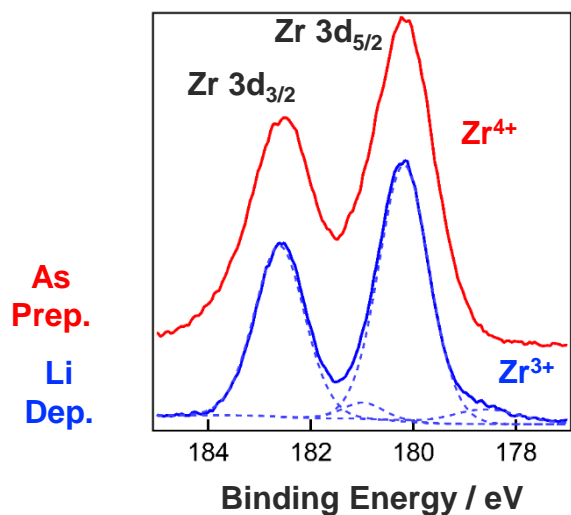


# Chemical Reactivity of Doped LLZO

*Nb-LLZO ( $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12}$ )*



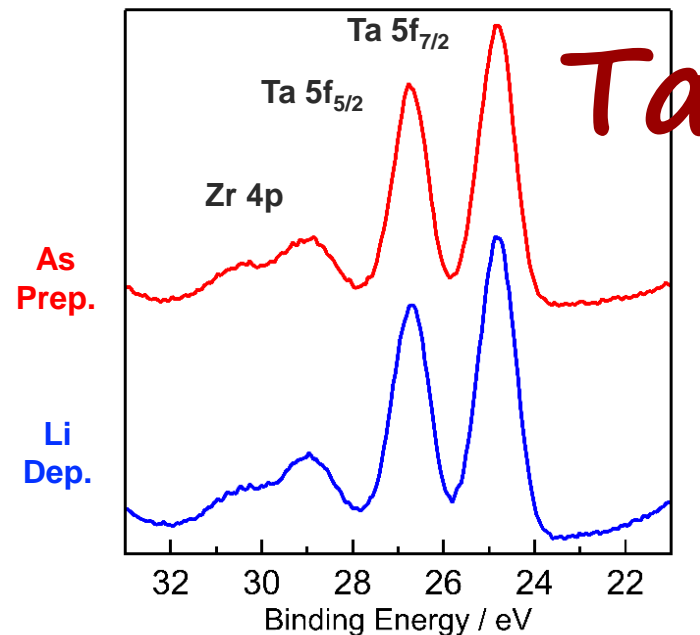
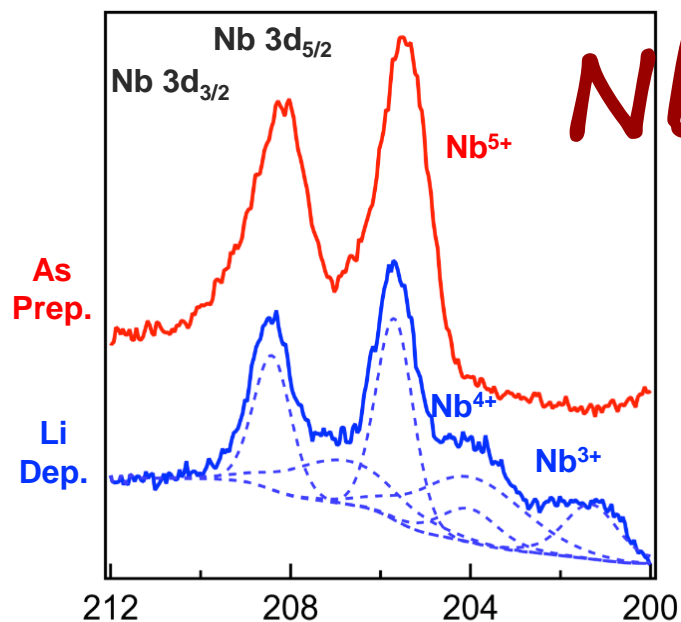
- Depositing Li on UHV annealed Nb-doped LLZO reveals similar instability of Nb<sup>5+</sup> to reduction by Li as for our model Nb-STO(*hkl*) system
- Slight reduction of Zr observed as well
- Small shift of La peak to lower binding energy



**Nb in doped LLZO is reduced by deposited Li**

# Effect of Doping on Interfacial Stability

*Nb-LLZO vs. Ta-LLZO*

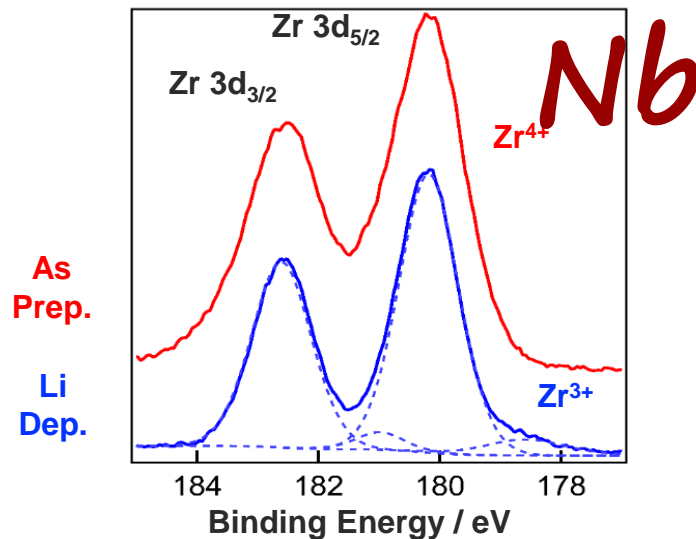


- Nb<sup>5+</sup> reduced to Nb<sup>4+</sup> and Nb<sup>3+</sup>
- No observed reactivity of Ta in contact with Li

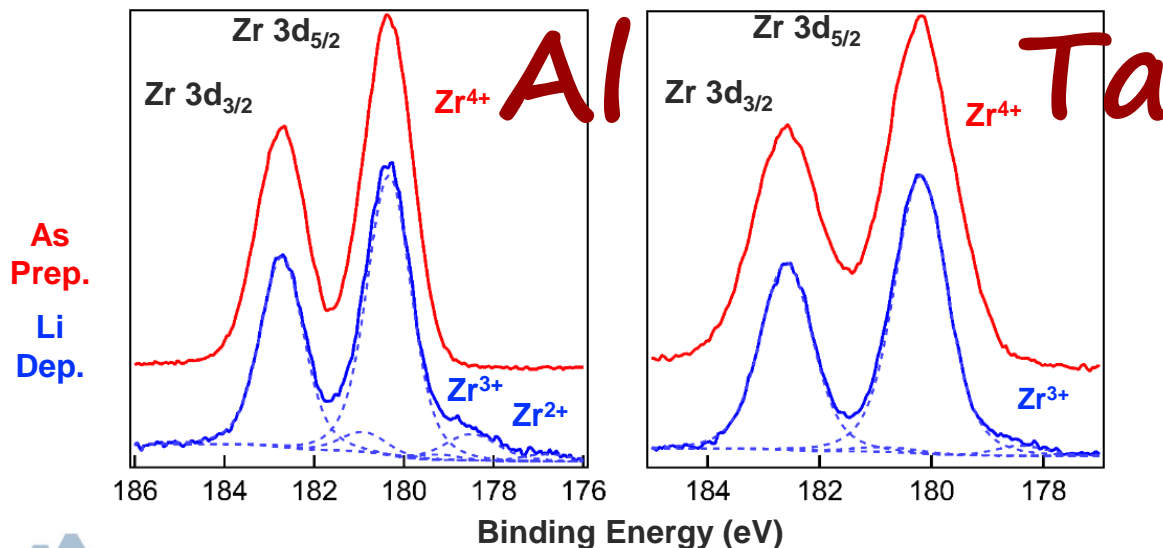
**Whether the reactivity of Nb-doped LLZO is surface-limited is subject of ongoing studies**

# Effect of Doping on Interfacial Stability

*Nb-LLZO vs. Ta-LLZO vs. Al-LLZO*

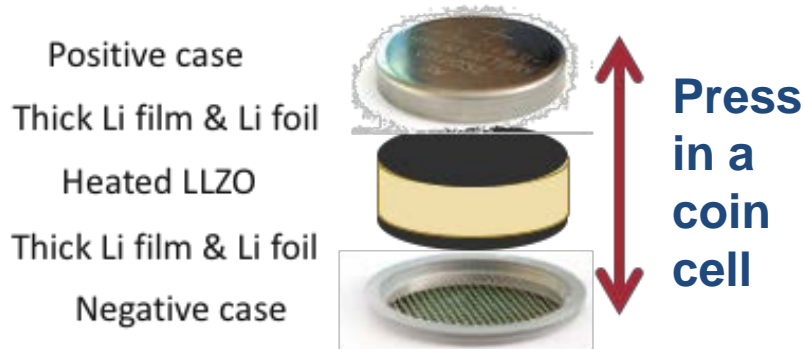


- Extent of Zr reduction varies across dopants, with Al exhibiting the highest degree of Zr reduction (~10% Zr<sup>3+</sup>)

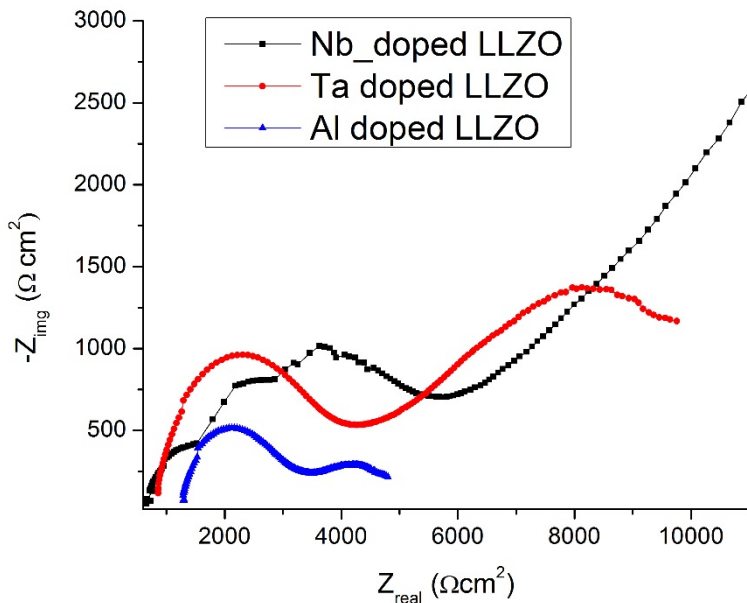


# Impedance of doped LLZO

## Impedance Measurement in Coin Cell



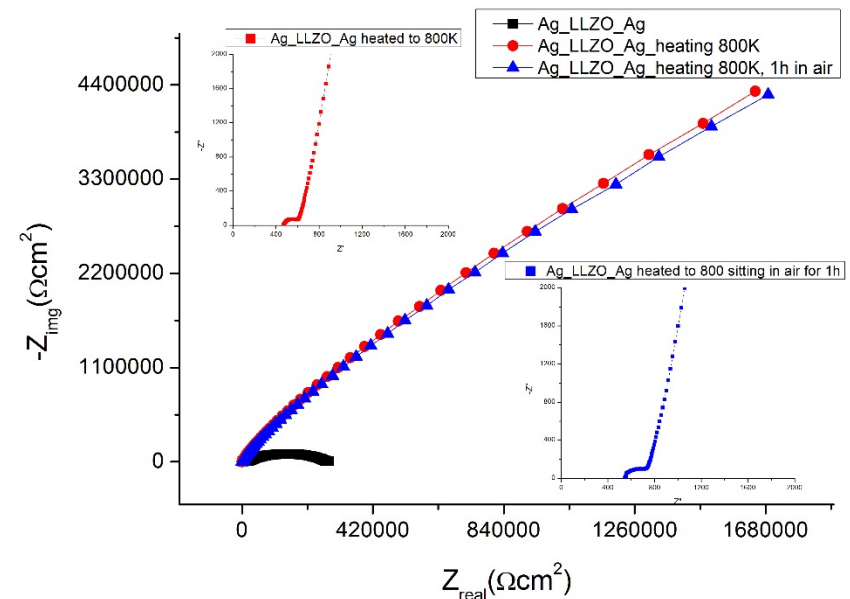
## Test with Ag Paste



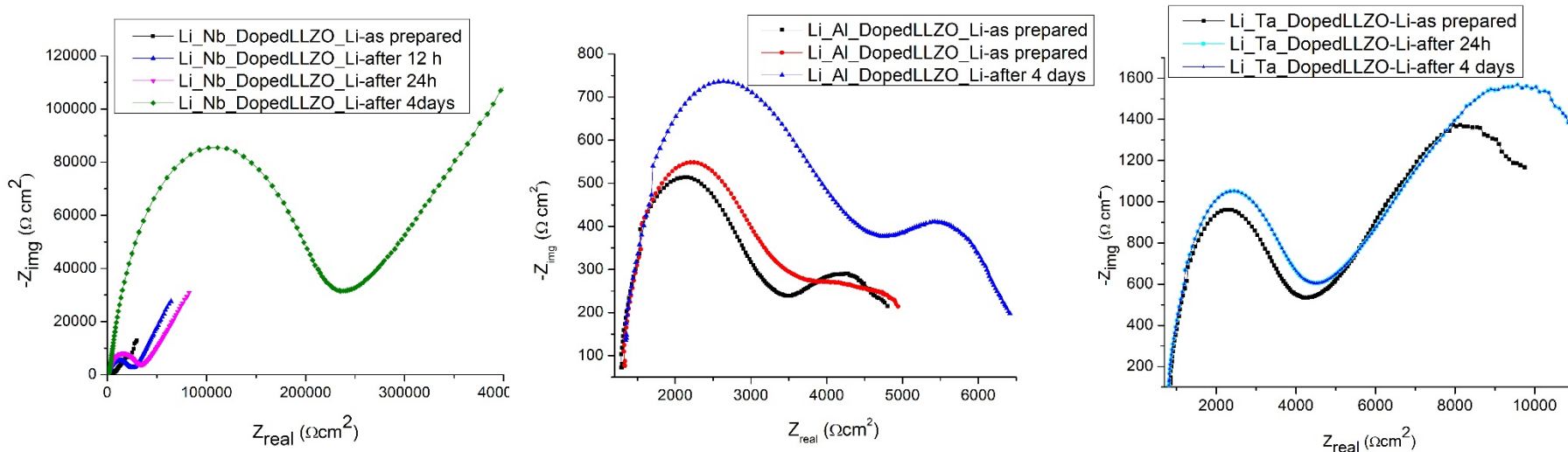
## Test with Ag Paste

Al doped LLZO :

- Ag paste on both sides of the pallet
- Typical Nyquist plot of the pallet sintered at 800°C (red and blue)
- Suppressed semicircle at high frequency can be attributed to the total (bulk and grain-boundary) contribution;
- A tail at low frequency is the blocking effect of the Ag paste.



# Change in Impedance of Li/doped LLZO with time



- *The impedance spectra include total resistance of the bulk and grain boundaries (first semicircle) and interfacial resistance (second semicircle)*
- **Nb doped LLZO**
  - *large impedance, and impedance grow with time*
- **Ta doped LLZO**
  - *Small Impedance, minimal change with time*

**Change in impedance correlates with the extent of reduction by Li**





# Response to last year reviewer's comments

**Comment:** The overall objectives are admirable—to advance our fundamental understanding of electrochemical interfaces. This reviewer's concern is that the experiments are too far afield from relevant systems. This reviewer has no objection to working with model systems, but the model systems should be chosen with more emphasis on relevance to practical systems. For example, the relevance of strontium titanate ( $\text{SrTiO}_3$ ) substrates is unclear. Also, the reviewer suggested that LiPON should be seriously considered as a model solid electrolyte system as it is the only “known good” material.

**Response:** We have chosen new model systems: LLTO for solid electrolyte and  $\text{LiCoO}_2$  for cathode materials instead of strontium titanate, which served as initial well-defined system. Currently we are moving from these model systems to doped LLZO and LPS, where we have established collaborations with Jeff Sakamoto and his group. In future, we plan to extend our studies and collaborations to study other electrolyte systems.

**Comment:** This reviewer is concerned that the materials being used here, such as the surface treatments and electrolytes and the nano-Li islands, bear little or no resemblance to the actual interfaces in Li batteries. The PI stated that one needs “well defined interfaces” to understand what is going on. The issue is that the Li interface appears to be very messy, and that is what we have to learn to deal with.

**Response:** We have made a transition to more realistic solid state electrolytes, LLZO and LPS. The methods that we use provide insights into how chemical reactivity and ion transport at the Li-solid interface affect battery functionality. We show that different surface treatments can be used to modify these properties, which could be applicable to the actual interfaces in Li batteries.



# Collaborations with other institutions and companies

- Jeff Sakamoto (UM)
  - Anode/Electrolyte interfaces, Li/LLZO

## Argonne MSD (Synthesis)

- Mercouri Kanatzidis
  - Synthesis and Characterization of Amorphous Materials
- John Mitchell
  - Synthesis and Characterization of Complex Oxide Materials



# Proposed Future Work

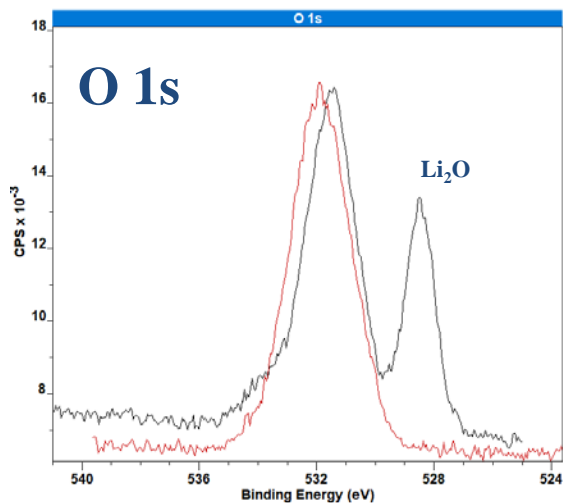
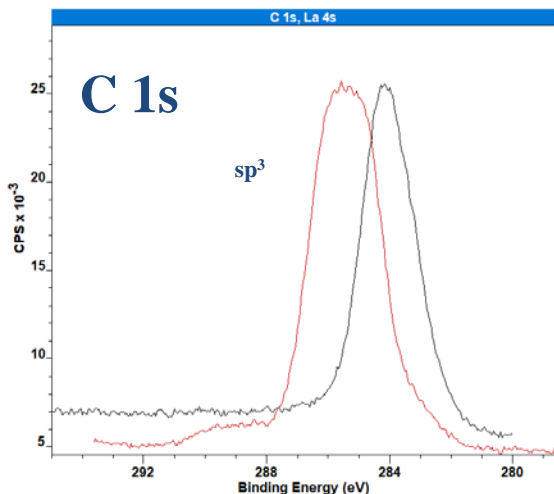
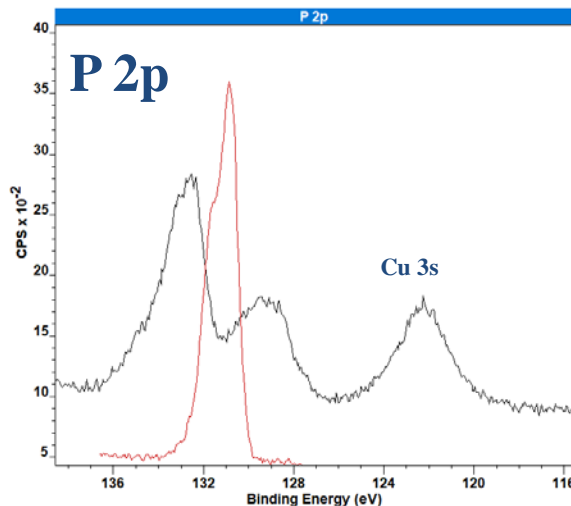
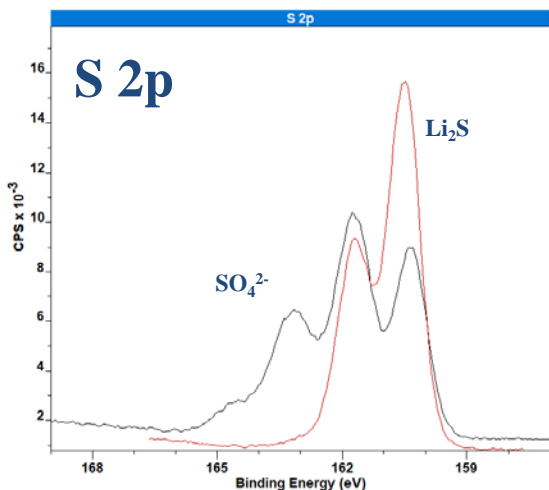
## ***Li-Solid Electrolyte systems:***

- Ion transport through the bulk and across heterogeneous interfaces, including grain boundaries.
- The role of strain (coherent XRD) and vacancy mobility.
- Stability of Li-electrolyte interfaces (chemical and mechanical).
- Transition from well-ordered systems to disordered systems

## ***Cathode-Solid Electrolyte systems:***

- Stability of cathode-electrolyte interfaces using experiment and theory
- Understanding origins of interfacial resistance
- The role of interfacial dopants

# Li<sub>3</sub>PS<sub>4</sub> preliminary work



- Sulfur seems oxidized after sputtering lithium
- Phosphorus is involved in reactions with Li
- Carbon peak is shifting, indicating carbon reduction by lithium
- Oxygen peak shows Li<sub>2</sub>O formation after sputtering



Red line before sputtering  
Black line after sputtering



# Summary

- Developed new synthesis and characterization tools for controlled deposition of lithium on solid electrolytes
- HAXPES of oriented Li/LLTO indicates that the amount of reduced Ti in LLTO is highly dependent on orientation
- Higher reactivity in Li/LLTO correlates with faster diffusion: need to optimize both together
- HAXPES of doped Li/LLZO indicates that Ta doped LLZO is stable while Nb-doped LLZO is reduced by deposited Li
- Impedance measurements indicate changes in resistivity are correlated with the extent of Li reduction.

